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Thermodynamic studies on metal complexes of Pb^{2+}, Zn^{2+}, Sr^{2+} and Mg^{2+} with 2-amino pyrimidine in water and water-acetonitrile binary solvent systems at 298.15 K, 308.15 K and 318.15 K by conductometric method

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ABSTRACT

Stability constants are measured for complexes of Pb^{2+}, Zn^{2+}, Sr^{2+} and Mg^{2+} with 2-amino pyrimidine (AMPYM) in pure water and water-acetonitrile binary solvent systems at 298.15, 308.15 and 318.15 K by conductometric method. The results shows that the stoichiometry of the complexes of AMPYM with all investigated metal ions in all binary solvent systems is 1:2 [ML_2]. The log K_f values of M^{2+}-AMPYM complexes in H_2O-ACN binary solvent systems decreases with increasing % of ACN and increased with the increase in percentage of water and also with increase in temperature. The value of formation constants obtained by spectrophotometry for the AMPYM with Pb^{2+}, Zn^{2+}, Sr^{2+} and Mg^{2+} at 298.15 K in pure water are in good agreement with the values obtained by conductometry for AMPYM with all the investigated metal ions at 298.15 K. The ΔH^0 and ΔS^0 of the complexation reaction in the different H_2O-ACN binary solvent systems were evaluated by the temperature dependence of the formation constants using a linear least square analysis according to van't Hoff equation.

Keywords: 2-amino pyrimidine, conductometry, spectrophotometry, stability constants, thermodynamic parameters, complexation.

INTRODUCTION

Conductometry is widely used method to study the formation constant of metal-ligand complexes as this method is less time consuming, eco-friendly, low cost and very important that one can calculate thermodynamic parameters. With the help of different parameters one can perform thermodynamic calculations properly[1-3]. By using conductometric method, researcher can investigate formation constant and can calculate most of all thermodynamic parameters. Important thermodynamic parameters like Gibb's free energy, enthalpy and entropy can also be determine with this method[3-5]. The stability of a complex is depends on temperature, physical properties and composition of solvents used, size and charge of the metal ion, type of metal ion, nature of ligand and counter ion. With the help of conductometric method the value of stability constant can be evaluated by GENPLOT computer program. The entropy and enthalpy change of the complexation reactions in the different binary solvent systems can be calculated by temperature dependence of the formation constant using a linear least square analysis according to van't Hoff equation. Pyrimidine and its derivatives are of great importance and have industrial and medicinal applications. Many of them possess great biological activity[6]. The coordination property of pyrimidine and its derivatives with metal ions is very important in understanding the role of the metal ions in biological systems. In this paper we have reported the formation constants of AMPYM with Pb^{2+}, Zn^{2+}, Sr^{2+} and Mg^{2+} in pure water and H_2O-ACN binary solvent systems at 298.15, 308.15 and 318.15 K. This study is very important to understand the composition of solvent system used, nature of the ligand, ionic size and effect of temperature.

MATERIALS AND METHOD

In the present investigations the reagents used were of analytical reagent grade and used without further purification. Lead nitrate ($Pb(NO_3)_2$), Magnesium nitrate ($Mg(NO_3)_2.6H_2O$) from Finar, Strontium nitrate ($Sr(NO_3)_2$) from central drug house pvt ltd, potassium chloride (KCL) from Merck limited, Mumbai, Zinc nitrate ($Zn(NO_3)_2.6H_2O$) were purchased from Molychem. 2 amino pyrimidine (AMPYM) was purchased from TCI. Acetonitrile extra pure was purchased from Finar Chemicals limited Ahmedabad. Conductivity water with conductivity less than 2.0×10^{-6} was used for preparation of all the solutions. Glassware used were thoroughly cleaned with freshly prepared aqua - regia and rinsed thoroughly with deionized water.

A digital Equiptronics conductivity apparatus Model EQ-665 was used to measure the conductance of the system, at a constant temperature within ±0.1°C using WENSAR thermostat, model WMS 300 with cell constant 1.02 cm^{-1} throughout the studies[9]. A double beam spectrophotometer (Kyoto, Japan) Model Shimadzu UV-1700 with matched 10 mm quartz cells was used for spectrophotometric measurements. A bandwidth of 1 nm was used and the wavelength accuracy was kept within ± 0.5 nm. The Shimadzu UV PC software version 2.0 was used for processing data. The spectra were recorded at a scan speed of 400 nm/min. Analytical balance model Sartorius GD503 (Bradford, MA, USA) having a readability of 0.0001 g was used for weighing the samples.

EVALUATION OF FORMATION CONSTANT (K_f)

Conductance measurements provide valuable information about the stoichiometry of the complexation reaction, it also provide information about the affinity of the ligand. For the conductance

of the solution measurement is carried out by titrating the metal salt solution with ligand solution in a suitable solvent system. The equilibrium can be described for a 1:1 metal- ligand binding is as follows;

$$M^+ + L = ML^+ \qquad (1)$$

Where, M^+, L, and ML^+ represent the free solvated cation, the free ligand, and the complex respectively. The formation constant of the complexation reaction is calculated using the following expression[7,8].

$$K_{ML^+} = \frac{\Lambda_{M^+} - \Lambda}{\Lambda - \Lambda_{ML}\left\{L]_t - \left(\frac{\Lambda_{M^+} - \Lambda}{\Lambda_{M^+} - \Lambda_{ML}}\right)[M]_t\right\}} \qquad (2)$$

where $[M]_t$, $[L]_t$, represent the concentration (in mol/L) of total cation, total ligand respectively and Λ_{M+}, Λ_{ML} and Λ represents the molar conductivities of the ligand free metal salt solution, the complexed cation solution at the same concentration and molar conductivities respectively.

RESULT AND DISCUSSION

The complexation of AMPYM with Pb^{2+}, Zn^{2+}, Sr^{2+} and Mg^{2+} in pure water and H_2O-ACN binary solvents were studied by the variation of molar conductance(Λ) versus the ligand$[L]_t$ to cation$[M]_t$ molar ratio ($[L]_t$ / $[M]_t$) at various temperatures. Typical series of molar conductance values as a function of $[L]_t$/ $[M]_t$ mole ratios in pure H_2O and H_2O-ACN (v/v % ACN =30/50/70) binary solvent systems are shown in Figure1-4. From figure 1–4, it is observed that, addition of AMPYM to metal ions (Pb^{2+}, Zn^{2+}, Sr^{2+} and Mg^{2+}) in pure H_2O and H_2O-ACN (v/v % ACN = 30/50/70) binary solvent systems at different temperatures results in an decrease in molar conductance by increasing the ligand concentration. It is observed that addition of AMPYM to lead ion solution at different temperatures results in a decrease in molar conductance. Thus indicates that (Pb^{2+} - AMPYM) complex is less mobile than free solvated lead cation. Similar behavior was observed for Zn^{2+}, Sr^{2+} and Mg^{2+} cations in various binary solvent systems.

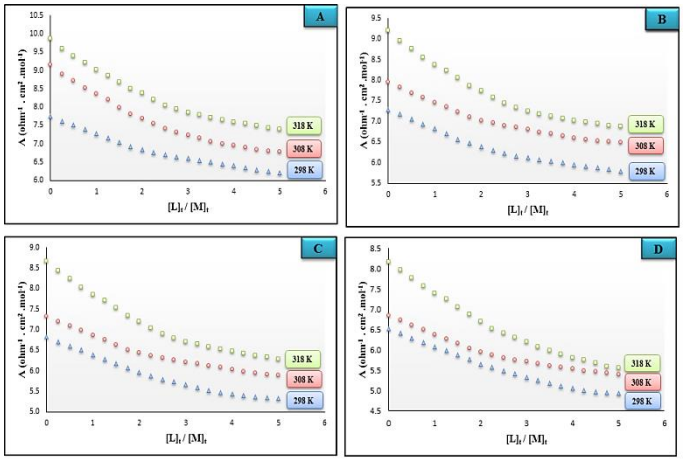

Figure 1 Molar conductance (ohm^{-1} cm^2 mol^{-1}) *vs.* AMPYM / [Pb^{2+}] plots in pure H_2O and H_2O–ACN binary solvent systems at various temperatures. v/v % of ACN in the binary solvent systems is: (A) 0% (B) 30 % (C) 50% and (D) 70%.

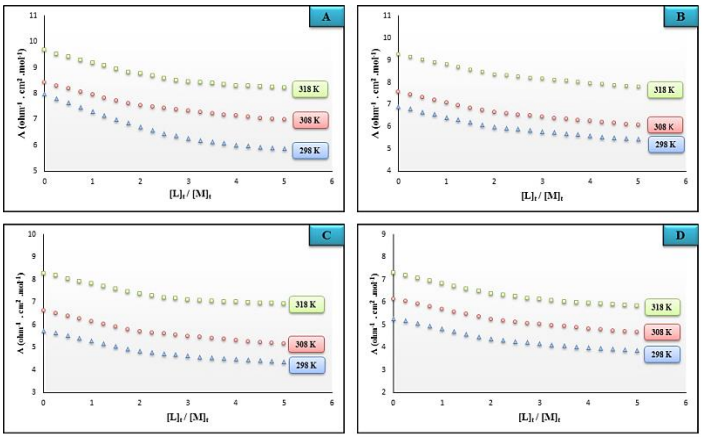

Figure 2 Molar conductance (ohm^{-1} cm^2 mol^{-1}) *vs.* AMPYM / [Zn^{2+}] plots in pure H_2O and H_2O–ACN binary solvent systems at various temperatures. v/v % of ACN in the binary solvent systems is: (A) 0% (B) 30 % (C) 50% and (D) 70%.

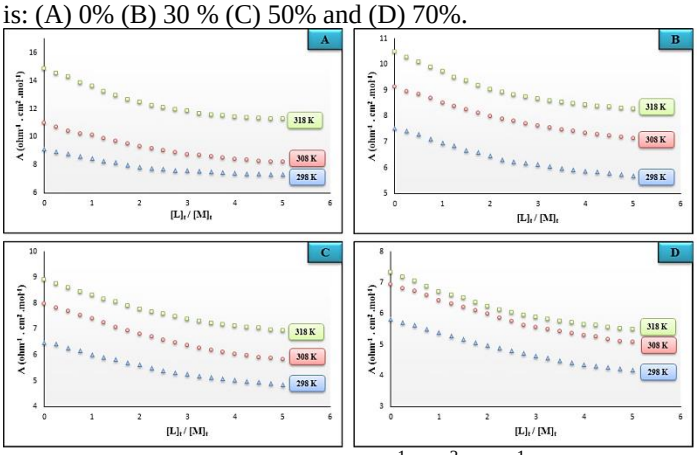

Figure 3 Molar conductance (ohm^{-1} cm^2 mol^{-1}) *vs.* AMPYM / [Sr^{2+}] plots in pure H_2O and H_2O–ACN binary solvent systems at various temperatures. v/v % of ACN in the binary solvent systems is: (A) 0% (B) 30 % (C) 50% and (D) 70%.

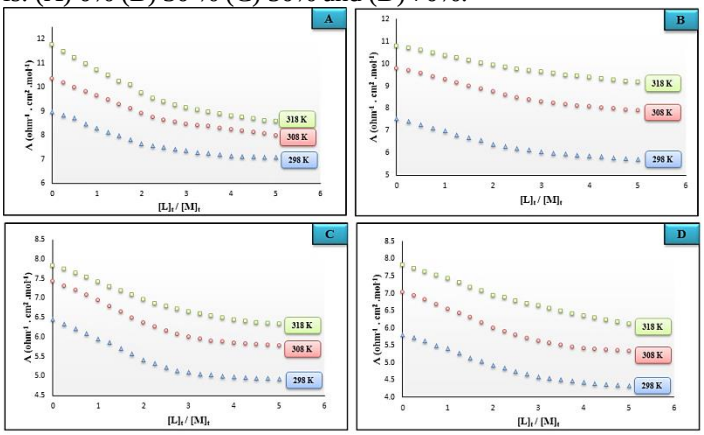

Figure 4 Molar conductance (ohm^{-1} cm^2 mol^{-1}) *vs.* AMPYM / [Mg^{2+}] plots in pure H_2O and H_2O–ACN binary solvent systems at various temperatures. v/v % of ACN in the binary solvent systems is: (A) 0% (B) 30 % (C) 50% and (D) 70%.

With the help of GENPLOT computer programme and from the variation of the molar conductance as a function of $[L]_t/[M]_t$ mole ratios the formation constant of the AMPYM at each temperature were calculated, The values of the formation constant[LogK_f] for the AMPYM-M^{2+} (M^{2+} = Pb^{2+}, Zn^{2+}, $Sr^{2+}$and Mg^{2+}) complexes in various binary solvent systems listed in Table-1.

In the present study it is observed that the formation constant values increases with increases in temperature. This indicates that the complexation reactions for AMPYM and metal ions (Pb^{2+}, Zn^{2+}, $Sr^{2+}$and Mg^{2+}) in pure H_2O and H_2O-ACN binary solvent systems are endothermic.

Table 1 LogKf values of AMPYM-M2+ complex in pure H2O and H2O-ACN binary solvent systems at different temperatures.

Complex	Solvent Medium	Log K_f ± SD		
		At 298.15 K	At 308.15 K	At 318.15 K
AMPYM – Pb^{2+}	Pure H_2O	4.20±0.04	4.23±0.06	4.26±0.05
	70% H_2O – 30% ACN[b]	4.16±0.06	4.19±0.04	4.22±0.03
	50% H_2O – 50% ACN	4.14±0.05	4.17±0.03	4.19±0.07
	30% H_2O – 70% ACN	4.12±0.07	4.14±0.05	4.16±0.06
AMPYM – Zn^{2+}	Pure H_2O	4.17±0.05	4.19±0.03	4.22±0.08
	70% H_2O – 30% ACN[b]	4.15±0.08	4.16±0.06	4.17±0.07
	50% H_2O – 50% ACN	4.11±0.04	4.12±0.08	4.14±0.04
	30% H_2O – 70% ACN	4.08±0.03	4.10±0.05	4.11±0.05
AMPYM – Sr^{2+}	Pure H_2O	4.16±0.03	4.18±0.05	4.20±0.07
	70% H_2O – 30% ACN[b]	4.14±0.06	4.16±0.04	4.18±0.05
	50% H_2O – 50% ACN	4.13±0.05	4.14±0.03	4.15±0.04
	30% H_2O – 70% ACN	4.12±0.04	4.13±0.04	4.14±0.08
AMPYM – Mg^{2+}	Pure H_2O	4.08±0.07	4.10±0.03	4.11±0.06
	70% H_2O – 30% ACN[b]	4.07±0.03	4.08±0.06	4.10±0.07
	50% H_2O – 50% ACN	4.05±0.05	4.06±0.05	4.08±0.05
	30% H_2O – 70% ACN	4.03±0.04	4.04±0.06	4.06±0.08

VAN'T HOFF PLOT FOR COMPLEXATION

With the help of the temperature dependence of the formation constants using a linear least squares analysis according to the van't Hoff equation, the ΔHo and ΔSo of the investigated complexation reactions in different H2O–ACN binary solvent systems were evaluated[9].

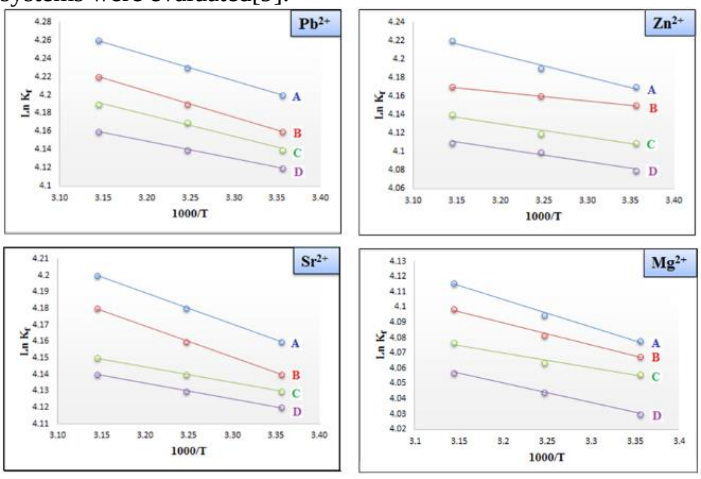

Figure 5 LnK_f *vs.*1000/T plots for the complexation of Pb^{2+}, Zn^{2+}, $Sr^{2+}$and Mg^{2+} ions with AMPYM in binary solvent systems: (A = Pure H_2O, B = 30% ACN, C = 50% ACN, D = 70% ACN)

The values of logK_f decrease with increase in the % of ACN in mixtures because in ACN molecule, it's nitrogen atom act as a soft base and metal-ligand complex behave as a soft acid and so it is strongly solvated by ACN molecules[10]. It is evident from the Table-I that the stability constant decrease by increase in the % of ACN with smaller Gutmann donor number (DN: ACN=14.1) in binary solvent systems.

In the present investigations, to support the results obtained from conductometric method, stoichiometry and formula constant of AMPYM-metal ion complexes have also been determined using spectrophotometric method, in which the mole ratio method was used. The analytical signals inceases with ligand mole fraction(or the mole ratio) until a maxima is reached. The maximum of the curve corresponding to the maximum formation of complex which indicates the ligand/metal ratio, which is the stoichiometry of the complex.

The absorption spectra of AMPYM, metal ion and its respective complexes in water in the wavelength range 200-400 nm are shown in Figure 6.

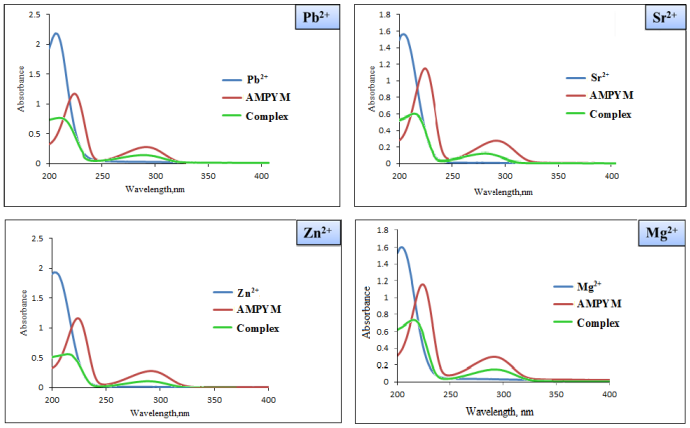

Figure 6. Absorption spectra of AMPYM, metal ions and their respective complexes in water.

Figure 7 shows the spectra of a series of solution of fixed concentration of metal ion and a variable concentration of AMPYM.

The mole ratio plots of absorbance vs. [AMPYM]/[M] at respective wavelengths where shifting occurred are presented in Figure 8. It can be seen that increasing [AMPYM]/[M] concentration ratio causes an increase in absorbance until this ratio reaches 1:2. Beyond this ratio the absorbance tends to level off for all four cations This indicates that the stoichiometry of the complexes formed is 1:2 (M:AMPYM) for all the cations.

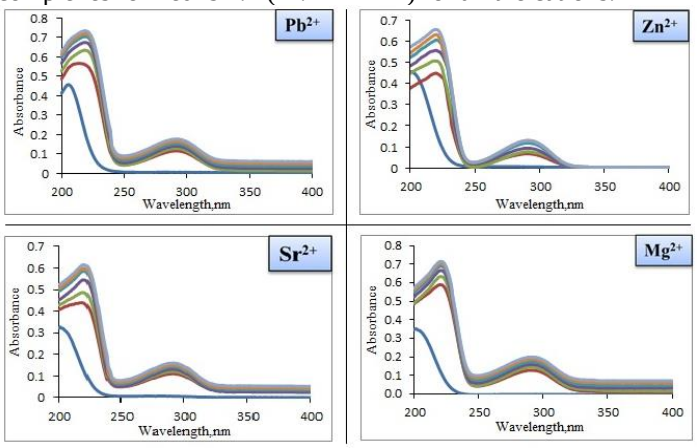

Figure 7. Overlaid absorption spectra of a series of water solutions containing a fixed concentration of metal ion (2.0 x 10-4) and varying concentration of ligand.

In the mole ratio method for determining the formation constant of 1:2 complexes, the following equations were employed as discussed previously.[50]

$$M + AMPYM \rightleftharpoons [M–AMPYM]\ (Complex) \quad \ldots (1)$$

$$K_{AMPYM} = \frac{[A/\varepsilon b]}{[C_M - A/\varepsilon_\lambda b] \times [C_{AMPYM} - A/\varepsilon b]} \quad \ldots (2)$$

Where; ε_λ = molar absorptivity, b = path length and A = absorbance at peak point.

Table II Comparison of formation constants for M^{2+}–AMPYM complexes at 298 K by spectrophotometry & conductometry.

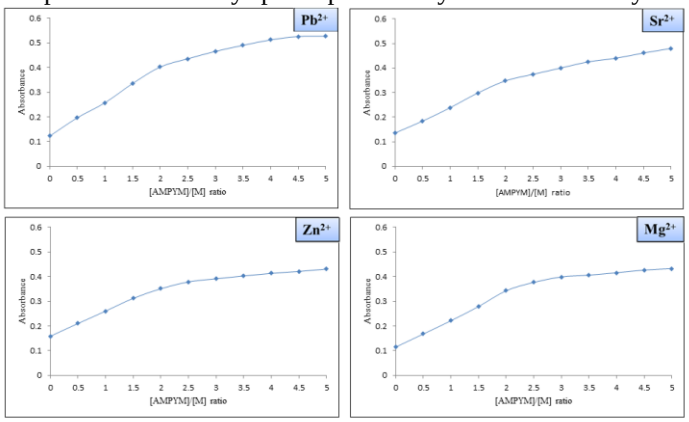

Figure 8. Spectrophotometric mole-ratio [AMPYM]/[M] plots for Pb^{+2}, Zn^{2+}, Sr^{2+} and Mg^{2+} in water at respective wavelength maxima at 298 K.

Table II Comparison of formation constants for M2+–AMPYM complexes at 298 K by spectrophotometry & conductometry.

Cation	λ_{max}	Log K_f ± SD at 298 K	
		Spectrophotometry [Molar-ratio method]	Conductometry
Pb^{2+}	219.0	4.201 ± 0.055	4.196 ± 0.025
Zn^{2+}	220.0	4.177 ± 0.025	4.174 ± 0.020
Sr^{2+}	220.0	4.145± 0.033	4.164 ± 0.044
Mg^{2+}	221.0	4.080 ± 0.036	4.078 ± 0.048

Table III Thermodynamic parameters for AMPYM-M2+ complexes in pure H2O and H2O–ACN binary solvent systems at 298.15 K.

Complex	Solvent Medium	ΔG^o± SD (kJ.mol^{-1})	ΔH^o ± SD (kJ.mol^{-1})	ΔS^o ± SD (J.mol^{-1}K^{-1})
AMPYM – Pb^{2+}	Pure H_2O	-23.96±0.08	5.44±0.1	98.67±2
	70% H_2O – 30% ACN[b]	-23.74±0.09	5.40±0.12	97.90±5
	50% H_2O – 50% ACN	-23.63±0.06	4.56±0.09	94.59±4
	30% H_2O – 70% ACN	-23.49±0.07	3.51±0.08	90.63±3
AMPYM – Zn^{2+}	Pure H_2O	-23.79±0.1	4.52±0.09	94.99±3
	70% H_2O – 30% ACN[b]	-23.69±0.09	1.74±0.1	85.35±4
	50% H_2O – 50% ACN	-23.45±0.08	2.80±0.09	88.11±3
	30% H_2O – 70% ACN	-23.25±0.1	3.02±0.1	88.21±2
AMPYM – Sr^{2+}	Pure H_2O	-23.76±0.08	3.01±0.09	89.79±3
	70% H_2O – 30% ACN[b]	-23.63±0.09	3.07±0.1	89.60±5
	50% H_2O – 50% ACN	-23.56±0.1	2.26±0.09	86.67±3
	30% H_2O – 70% ACN	-23.50±0.09	1.72±0.11	84.62±6
AMPYM – Mg^{2+}	Pure H_2O	-23.28±0.09	2.73±0.08	87.31±5
	70% H_2O – 30% ACN[b]	-23.21±0.1	2.81±0.1	87.29±7
	50% H_2O – 50% ACN	-23.11±0.09	2.43±0.09	85.70±6

	30% H_2O – 70% ACN	-22.99±0.08	2.46 ±0.1	85.48±7

[b]Composition of binary mixtures is expressed in v/v % for each solvent system;
SD=standard deviation

Table–II summarizes the mean values of formation constants (average of three determinations) obtained from mole ratio for UV–visible spectrophotometry. Further, the value of formation constants obtained by spectrophotometry for the AMPYM with Pb^{2+}, Zn^{2+}, Sr^{2+} and Mg^{2+} at 298.15 K in pure water are in good agreement with the values obtained by conductometry for AMPYM with all the investigated metals at 298.15 K. Further, the order of stability for all complexes was also identical with both the techniques, $Pb^{2+} > Zn^{2+} > Sr^{2+} > Mg^{2+}$.

The results which are summarized in Table-III shows that in all the cases, the complexation reactions between AMPYM and the studied metal cations in H_2O–ACN binary solvent systems, the obtained positive value of ΔH_o indicates that enthalpy is not the driving force for the formation of the complexes. Furthermore, the positive value of ΔS_o indicates that the entropy is responsible for the formation of the complexes.

So that the stability constant for all the investigated metal ions with ACN in all the binary solvent systems are entropy stabilized and enthalpy destabilized. According to the data in the table-III, the thermodynamic quantities are very sensitive to the composition and the nature of the mixed solvent and non-monotonic behavior is observed for the variation of enthalpy and entropy changes with the composition of the H_2O-ACN binary solvent systems[11].

EFFECT OF SOLVENT ON COMPLEXATION:

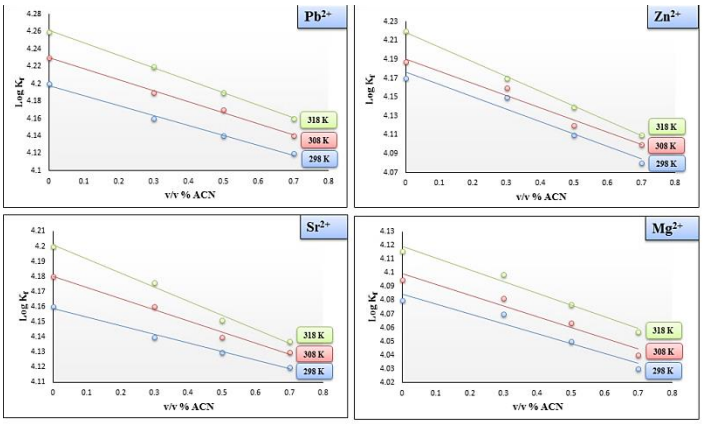

Figure 9 Changes of the stability constant ($logK_f$) of AMPYM-Pb^{2+}, AMPYM-Zn^{2+}, AMPYM-Sr^{2+} and AMPYM-Mg^{2+} complex with the composition of H_2O-ACN binary systems at different temperatures.

From Figure 9 (a,b,c,d) show the changes in the stability constant ($logK_f$) of AMPYM with Pb^{2+}, Zn^{2+}, Sr^{2+} and Mg^{2+} complexes versus the composition of pure H_2O and H_2O–ACN binary solvent systems at various temperatures. It is interesting to note that the formation constants of AMPYM–M^{2+} (M = Pb, Zn, Sr, Mg) complexes decreases with increase in the percentage of acetonitrile in H_2O–ACN binary solvent systems.

EFFECT OF IONIC SIZE ON COMPLEXATION

The variation of $logK_f$ versus the ionic radius in H_2O–ACN binary solvent systems at different temperatures for the formation of complexes of AMPYM with all the investigated metal ions are shown in Figure 10.The selection order of AMPYM with the cations Pb^{2+}, Zn^{2+}, Sr^{2+} and Mg^{2+} in binary solvents systems H_2O–ACN at 298.15, 308.15 and 318.15 K are $Pb^{2+}>Zn^{2+}>Sr^{2+}>Mg^{2+}$. It is evident from the figure that the order of selectivity of $logK_f$ of these complexes at 298.15, 308.15 and 318.15 K was AMPYM-Pb^{2+} > AMPYM-Zn^{2+} > AMPYM-Sr^{2+} > AMPYM-Mg^{2+}. Similar selectivity order was observed for all the compositions of binary solvent systems.

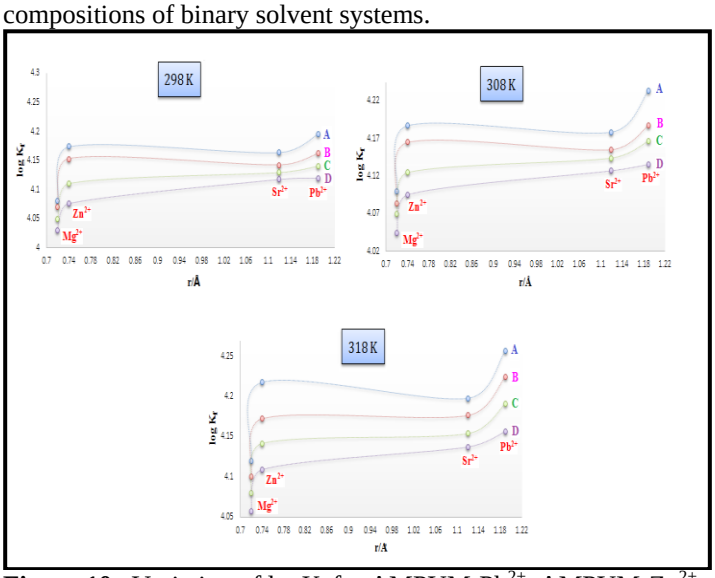

Figure 10 Variation of $logK_f$ for AMPYM-Pb^{2+}, AMPYM-Zn^{2+}, AMPYM-Sr^{2+} and AMPYM-Mg^{2+} complexes versus cationic radius in H_2O–ACN binary solvent systems (A = Pure H_2O, B = 30% ACN, C = 50% ACN, D = 70% ACN) at various temperatures.

CONCLUSION

The stability constant for the complexation of cations (Pb^{2+}, Zn^{2+}, Sr^{2+}, Mg^{2+}) with AMPYM in pure H_2O and H_2O-ACN binary solvent systems were determined conductometricaly at different temperatures. In most of the cases, the stability constant of the complex increased with the increase in percentage of water and with temperature. In the present study, in all the cases AMPYM formed 1:2 [ML_2] complex. The negative values of ΔG show the ability of the AMPYM ligand to form stable complexes and that the process is spontaneous. However, the obtained positive value of ΔH indicates that enthalpy is not driving force for the formation of the complexes. Furthermore, the positive value of ΔS indicates that entropy is a driving force for the complexation reaction. The value of formation constants obtained by spectrophotometry for the AMPYM with Pb^{2+}, Zn^{2+}, Sr^{2+} and Mg^{2+} at 298.15 K in pure water are in good agreement with the values obtained by conductometry for AMPYM with all the investigated metal ions.

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